X-ray and Neutron Science Excerpts from NXS

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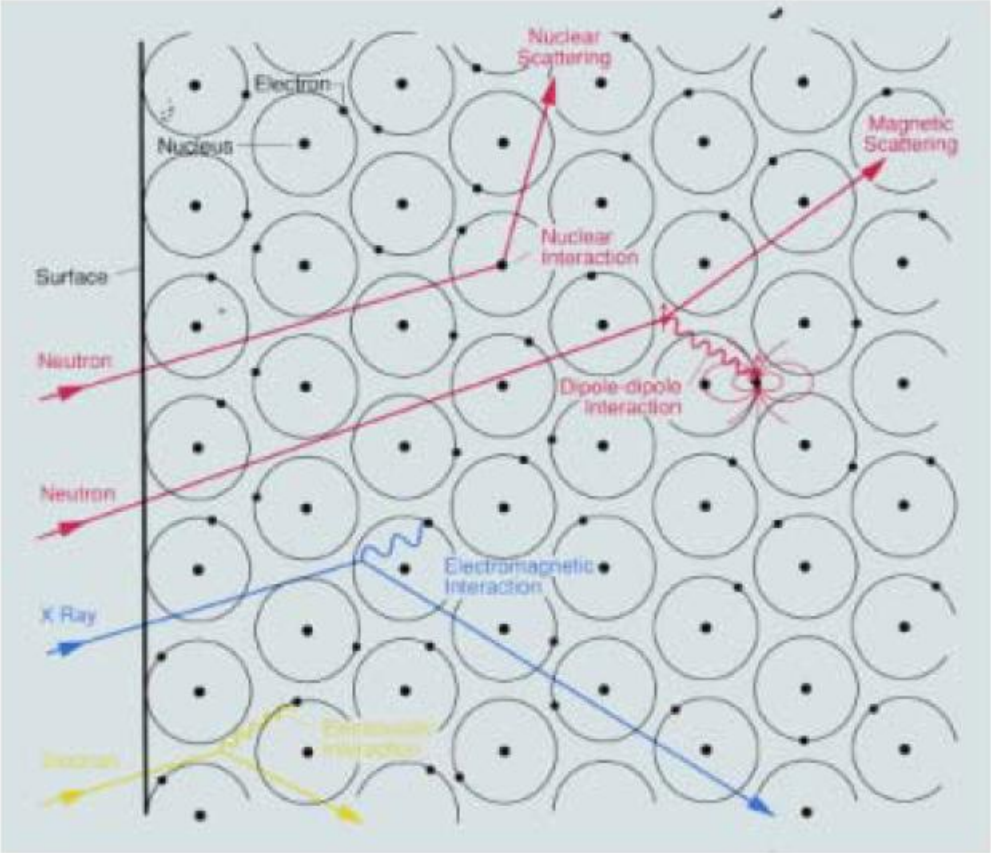
Advantages of Neutrons and X-Rays

- Penetrating/ Non Destructive N (X)
- Right wavelength/energy N,X
- Magnetic probe N,X
- Contrast matching N
- Weakly interacting-Born approxn. N,X
- *Global* Statistical information N,X
- Buried Interfaces—depth dependence N,X
- Impervious to sample environmental conditions, magnetic fields, etc.

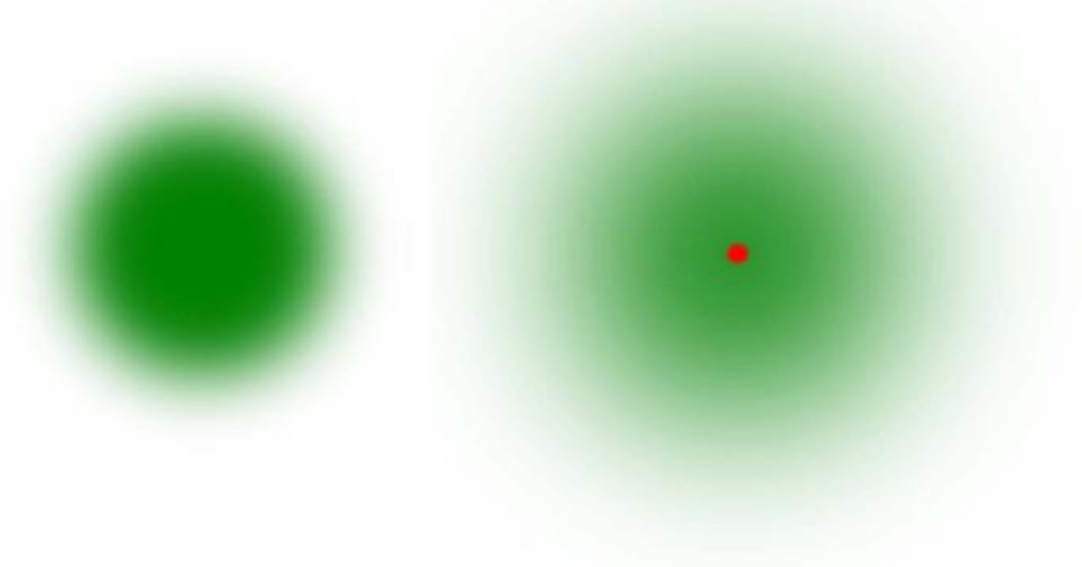
Interaction Mechanisms



- Neutrons interact with atomic nuclei via very short range (~fm) forces.
- Neutrons also interact with unpaired electrons via a magnetic dipole interaction.

What the particle sees….

$\rho_e(\underline{r})$ $V(\underline{r})$ m_n, $\underline{J}$



x-ray electron neutron

Thermal Neutrons (continuous)

Advantages

1) λ_n ~ Interatomic Spacing

2) Penetrates Bulk Matter (neutral particle)

3) Strong Contrasts Possible (e.g. H/D)

4) E_n ~ Elementary Excitations (phonons, magnons, etc.)

5) Scattered Strongly by Magnetic Moments

Disadvantages

1) Low Brilliance of Neutron Sources-Low Resolution or Intensities; Large Samples; Low Coherence; Surfaces Difficult

2) Some Elements Strongly Absorb (e.g. Cd, Gd, B)

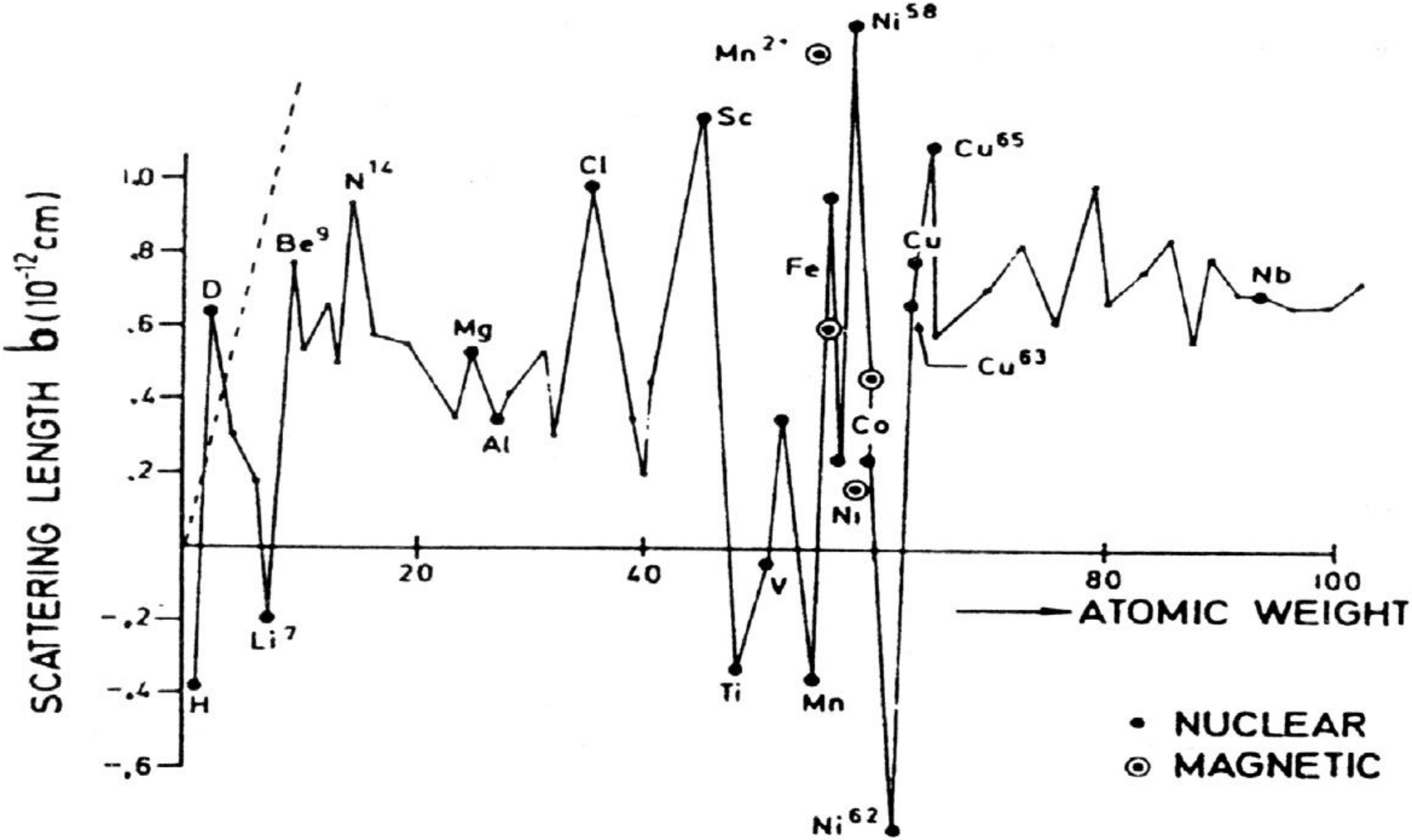
3) Kinematic Restriction on Q for Large E Transfers

4) Restricted to Excitations ≤ 100 meV

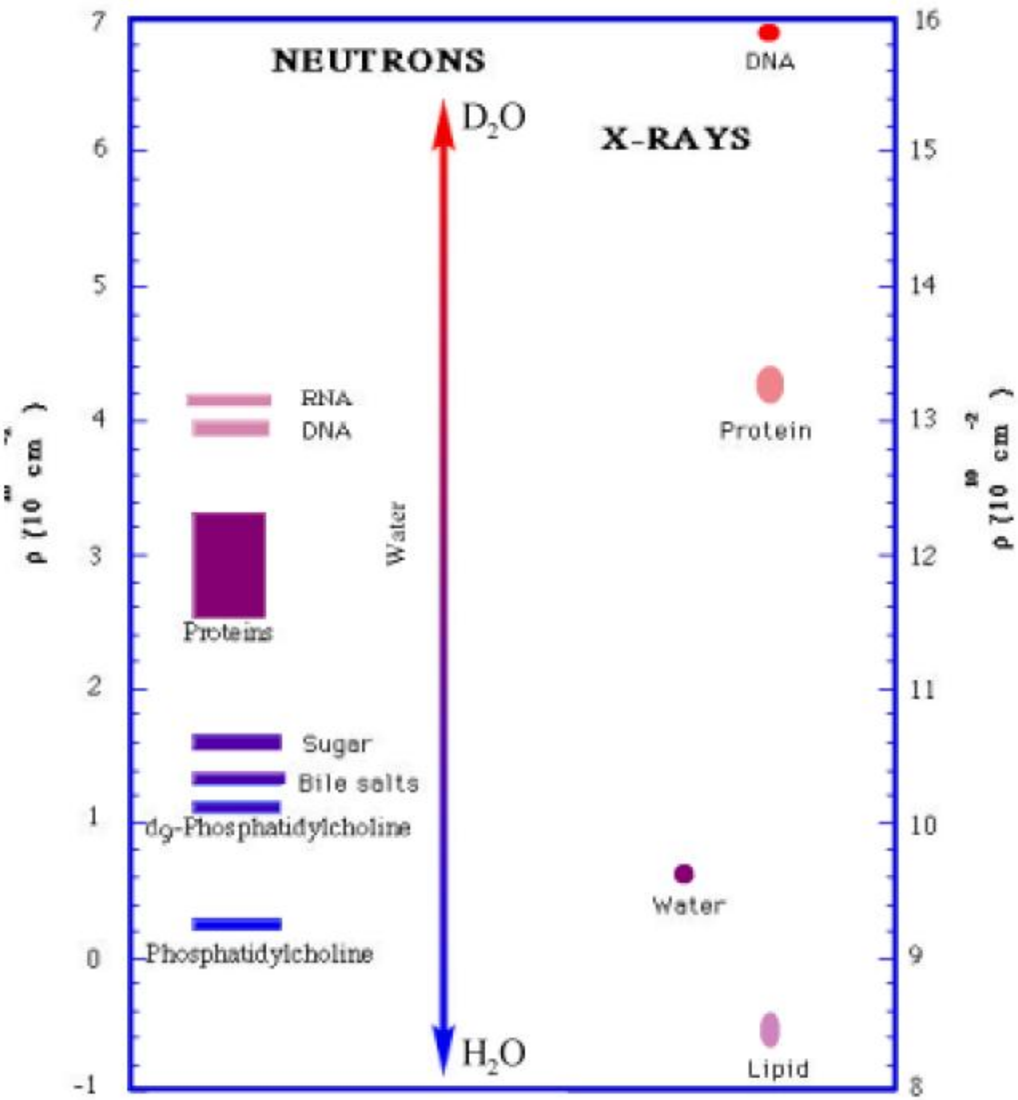
Spallation Neutrons (pulsed)

- Higher Brilliance
- Use all neutron via time of flight separation

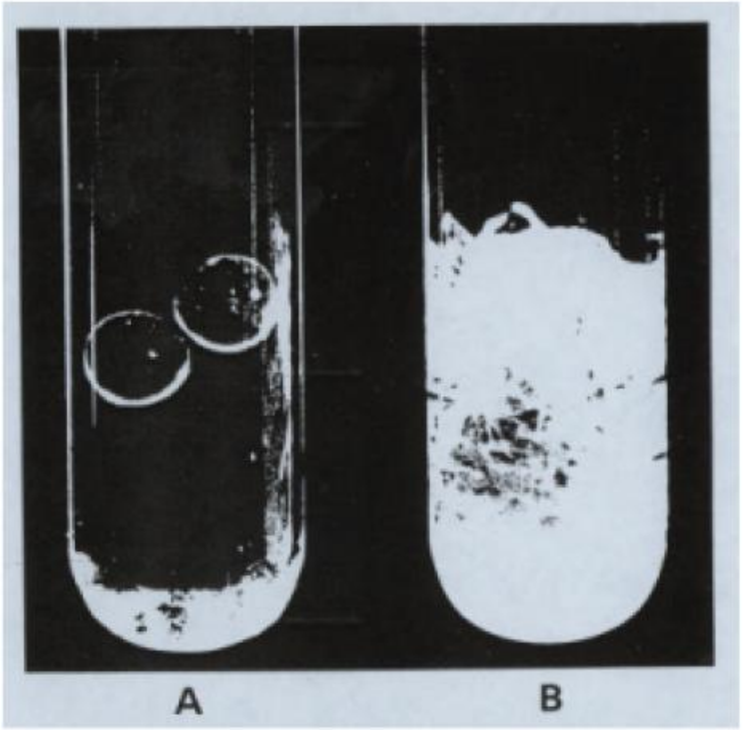
Intrinsic Cross Section: Neutrons



Contrast & Contrast Matching



* Chart courtesy of Rex Hjelm



Both tubes contain borosilicate beads + pyrex fibers + solvent. (A) solvent refractive index matched to pyrex;. (B) solvent index different from both beads and fibers – scattering from fibers dominates

Synchrotron X-rays

Advantages

1) λ_n - Interatomic Spacing

2) High Brilliance of X-ray Sources - High Resolution; Small Samples; High Degree of Coherence

3) No Kinematic Restrictions (E,Q uncoupled)

4) No Restriction on Energy Transfer that Can Be Studied

Disadvantages

1) Strong Absorption for Lower Energy Photons

2) Little Contrast for Hydrocarbons or Similar Elements

3) Weak Scattering from Light Elements

4) Radiation Damage to Samples

Scatttering by a Single Free Electron

el. accelern $\rightarrow$ $\bar{a} = \frac{e}{m}\bar{E}_0$

Radiated field $\rightarrow$ $\bar{E}_S^j = \frac{e}{c^2 R} e^{ikR}\left(\bar{a} \cdot \bar{\varepsilon}_j\right)\bar{E}j$

$$= \left(\frac{e^2}{mc^2}\right)\frac{e^{ikR}}{R}\left(\bar{E}_0 \cdot \bar{\varepsilon}_j\right)\bar{\varepsilon}_j$$

$$b = \left(\frac{e^2}{mc^2}\right)\left(\bar{\varepsilon}_i \cdot \bar{\varepsilon}_j\right)$$

- $R^2 \left|\frac{E_{scat}^j}{E_{in}}\right|^2 \rightarrow \frac{d\sigma}{d\Omega} = \underbrace{\left(\frac{e^2}{mc^2}\right)^2}_{r_0^2}\left[\frac{1 + \mathrm{Cos}^2(2\theta)}{2}\right]$ ← "Polarization Factor"

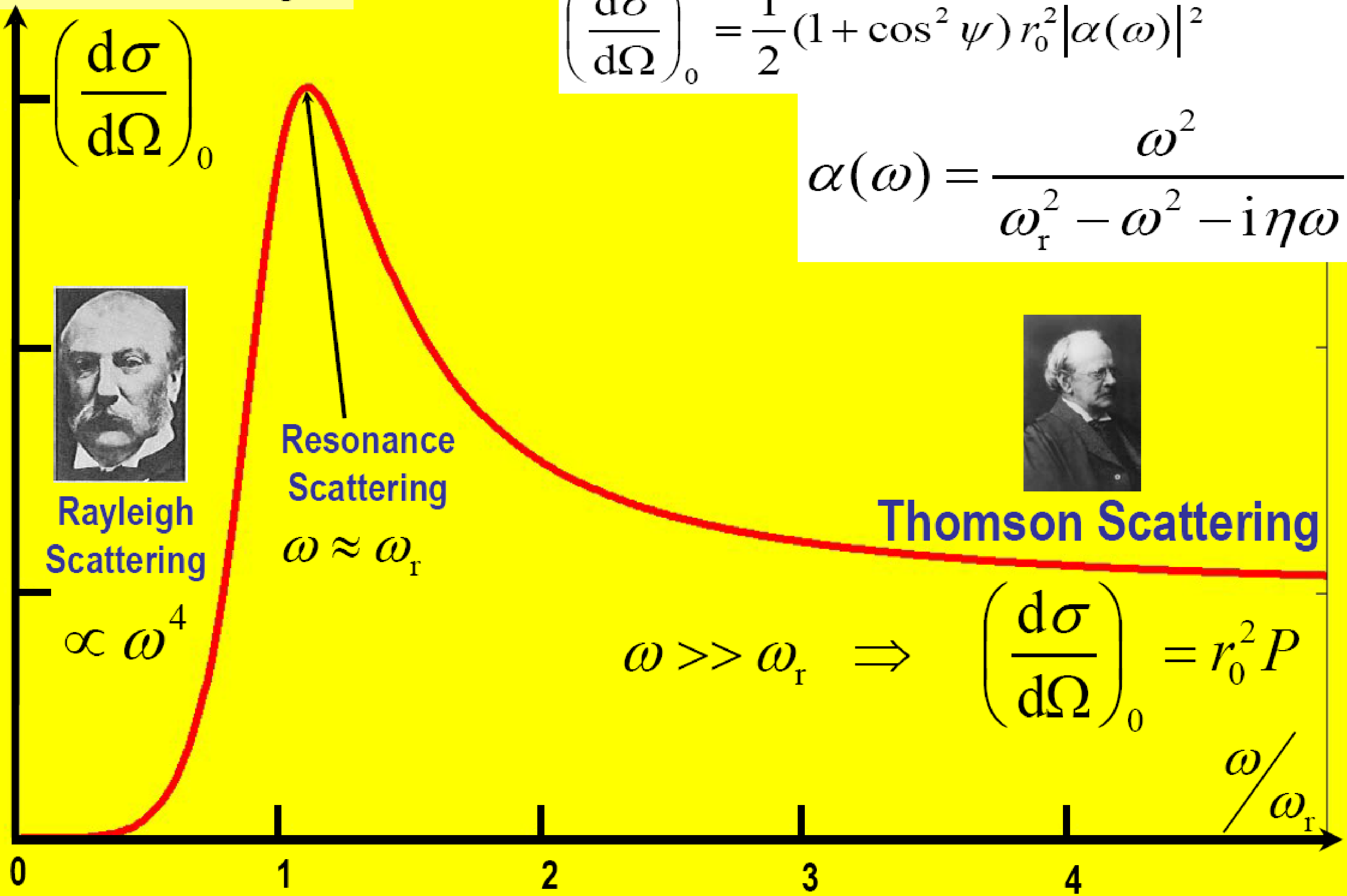
r_0^2 ← effective cross section of electron

Intrinsic Cross Section: X-Rays

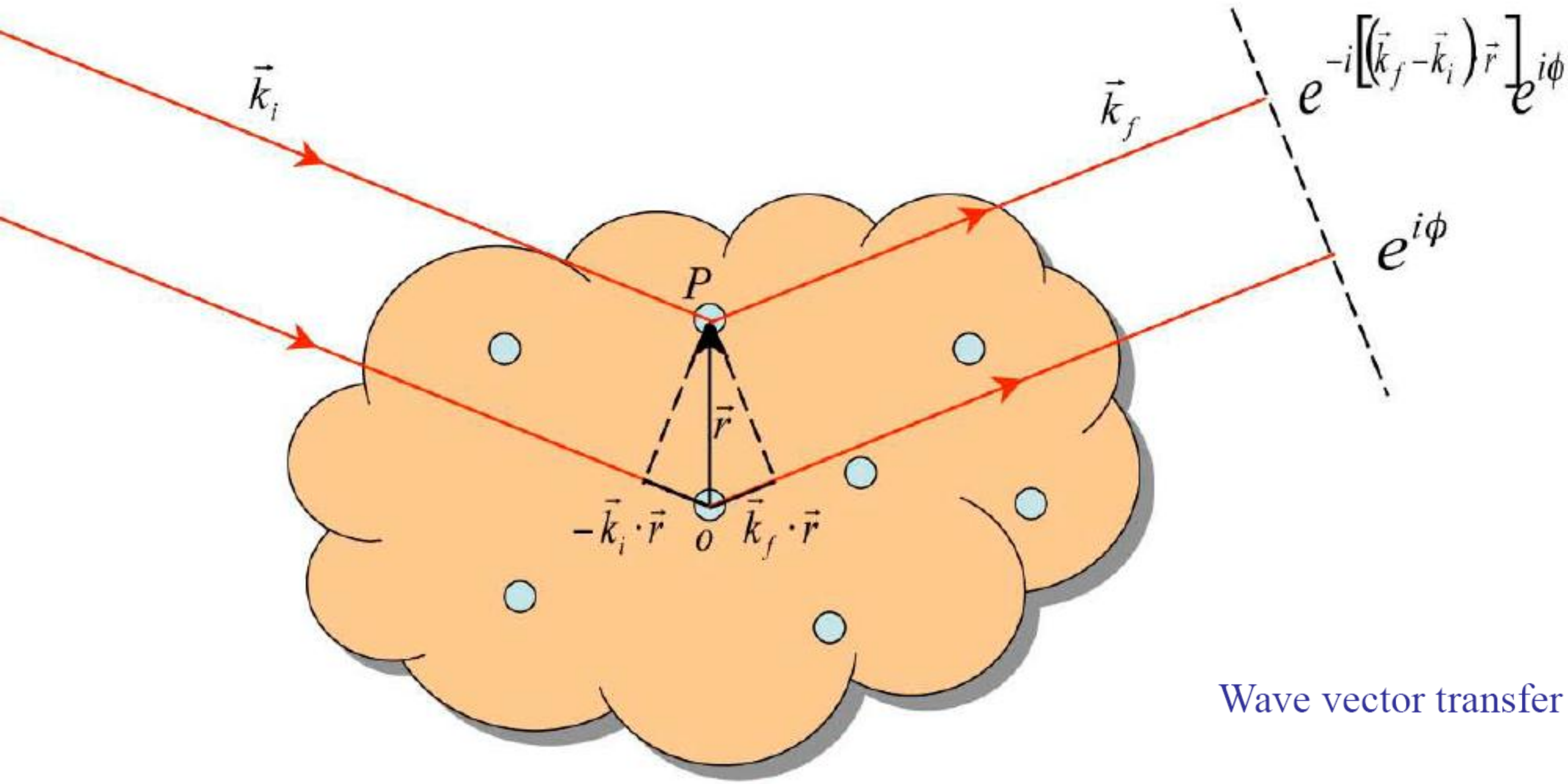
$$\left|\frac{E_{\mathrm{rad}}(R,t)}{E_{\mathrm{in}}}\right|^2 = \frac{r_0^2}{R^2}\left|\alpha(\omega)\right|^2 P(\psi) = \frac{\left|f(\Omega)\right|^2}{R^2}$$

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_0 = \frac{1}{2}(1+\cos^2\psi)\, r_0^2\left|\alpha(\omega)\right|^2$$

$$\alpha(\omega) = \frac{\omega^2}{\omega_{\mathrm{r}}^2 - \omega^2 - \mathrm{i}\eta\omega}$$



Adding up phases at the detector of the wavelets scattered from all the scattering centers in the sample:



Wave vector transfer is defined as

$$\mathbf{q} = \mathbf{k_f} - \mathbf{k_i}$$

Neutrons

Sum of scattered waves on plane II:

$$\psi_{se} = Ae^{i\phi}\sum_i \frac{b_i}{R} e^{-i\vec{q}\cdot\vec{R}_i}$$

$$\frac{d\sigma}{d\Omega} = \frac{vdS|\psi_{se}|^2}{v|A|^2\, d\Omega} = \frac{vdS}{v|A|^2}\frac{|A|^2}{R^2}\frac{1}{d\Omega}\sum_{ij} b_i b_j\, e^{-i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}$$

$$= \sum_{ij} b_i b_j\, e^{-i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)}$$

X-rays

$$\frac{d\sigma}{d\Omega} = r_0^2 \sum_{ij} e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)} \times \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right)$$

$\vec{r}_i \rightarrow$ electron coordinates

In most cases, we must do a thermodynamic or ensemble average (for incoherent beam)

X-rays

$$\frac{d\sigma}{d\Omega} = r_0^2\left[\frac{1 + \mathrm{Cos}^2(2\theta)}{2}\right] S(\mathbf{q})$$

$$S(\mathbf{q}) = \langle \Sigma_{ij} \exp[-i\mathbf{q}.(\mathbf{r}_i - \mathbf{r}_j)]\rangle$$

Intensity of Structure Factor

$\{\mathbf{r}_i\}$ == electron positions.

$\Sigma_i \exp[-i\mathbf{q}.\mathbf{r}_i] = \rho_{el}(\mathbf{q})$ Fourier Transform of electron density
And, for x-rays, $S(\mathbf{q}) = \langle \rho_{el}(\mathbf{q}) \rho_{el}^*(\mathbf{q}) \rangle$

If electrons are bound to atoms centered on $\vec{R}_i$

$$\rho_{el}(\vec{r}) = \sum_i f_{el}(\vec{r} - \vec{R}_i)$$

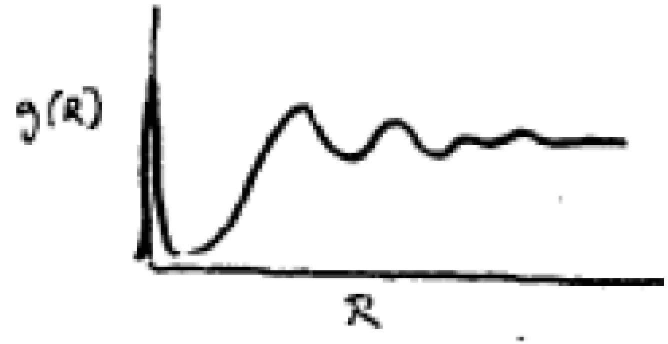
$$\rho_{el}(\vec{q}) = \int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}} \sum_i f(\vec{r} - \vec{R}_i)$$

$$= \sum_i \left[\int d\vec{r}\, e^{-i\vec{q}\cdot(\vec{r}-\vec{R}_i)} f(\vec{r} - \vec{R}_i) \right] e^{-i\vec{q}\cdot\vec{R}_i}$$

$$= Zf(\vec{q}) \sum_i e^{-i\vec{q}\cdot\vec{R}_i} = Zf(\vec{q})\rho_N(\vec{q})$$

atomic form factor

$S(q)=\left\langle\left|\rho_N(\vec{q})\right|^2\right\rangle \qquad \left[\times\left|f(q)\right|^2\right]$ for x–rays



$\rho_N(\vec{q})=\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\rho_N(\vec{r})$

$\Rightarrow S(q)=\iint d\vec{r}\, d\vec{r}\,' e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')}\left\langle\rho_N(r)\rho_N(r')\right\rangle$

If $\left\langle\rho_N(\vec{r})\rho_N(r')\right\rangle$ = Fn. of $(r-r')$ only,

$S(q)=V\int d\vec{r}\,' e^{-i\vec{q}\cdot\vec{R}}\left\langle\rho_N(\vec{r})\rho_N(\vec{r}-\vec{R})\right\rangle$

$=\int d\vec{R}\, e^{-i\vec{q}\cdot\vec{R}}g(\vec{R})$

- $g(\vec{R})$ = Pair-distribution function

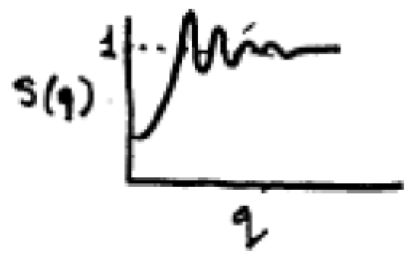
$=V\left\langle\rho_N(\vec{r})\rho_N(\vec{r}-\vec{R})\right\rangle$

$\Rightarrow$ Probability that given a particle at $\vec{r}$, there is distance $\vec{R}$ from it (per unit volume)

$g(\vec{R})=\delta(\vec{R})+g_d(\vec{R}) \qquad S(q)-1=\int d\vec{R}\, e^{-i\vec{q}\cdot R}g_d(\vec{R})$

$g_d(\vec{R})_{R\to\infty}\to V\langle\rho\rangle^2$

Liquids and Glasses

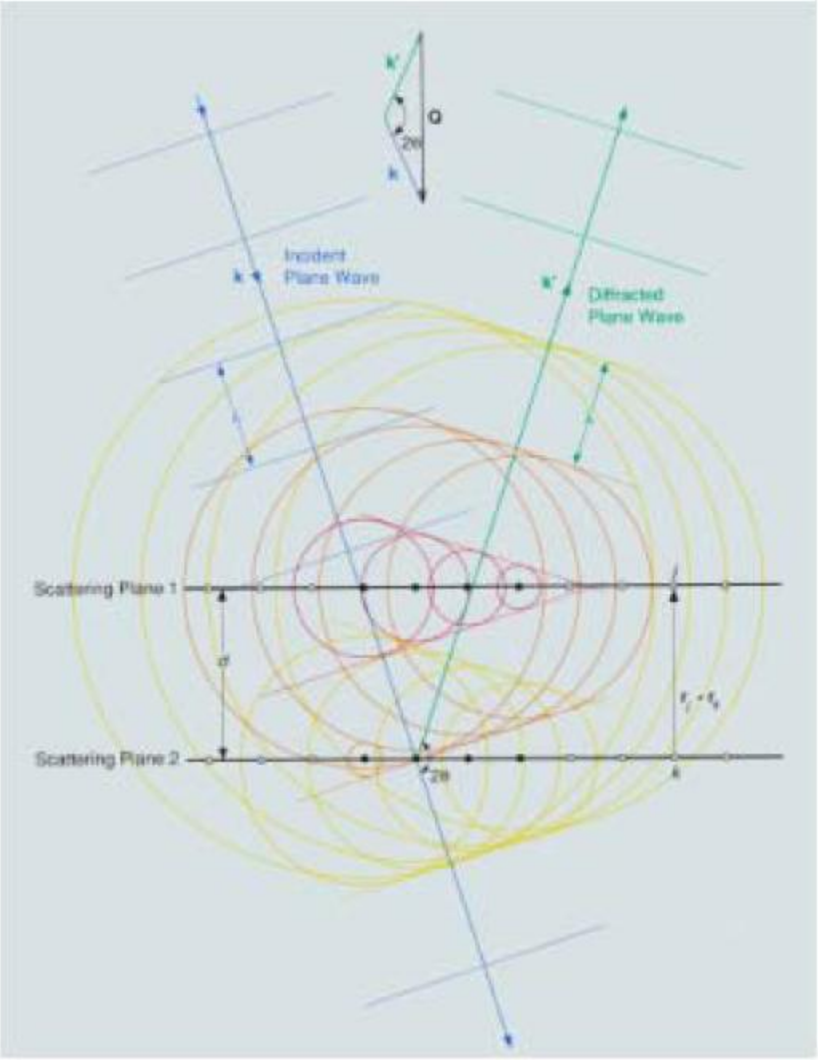


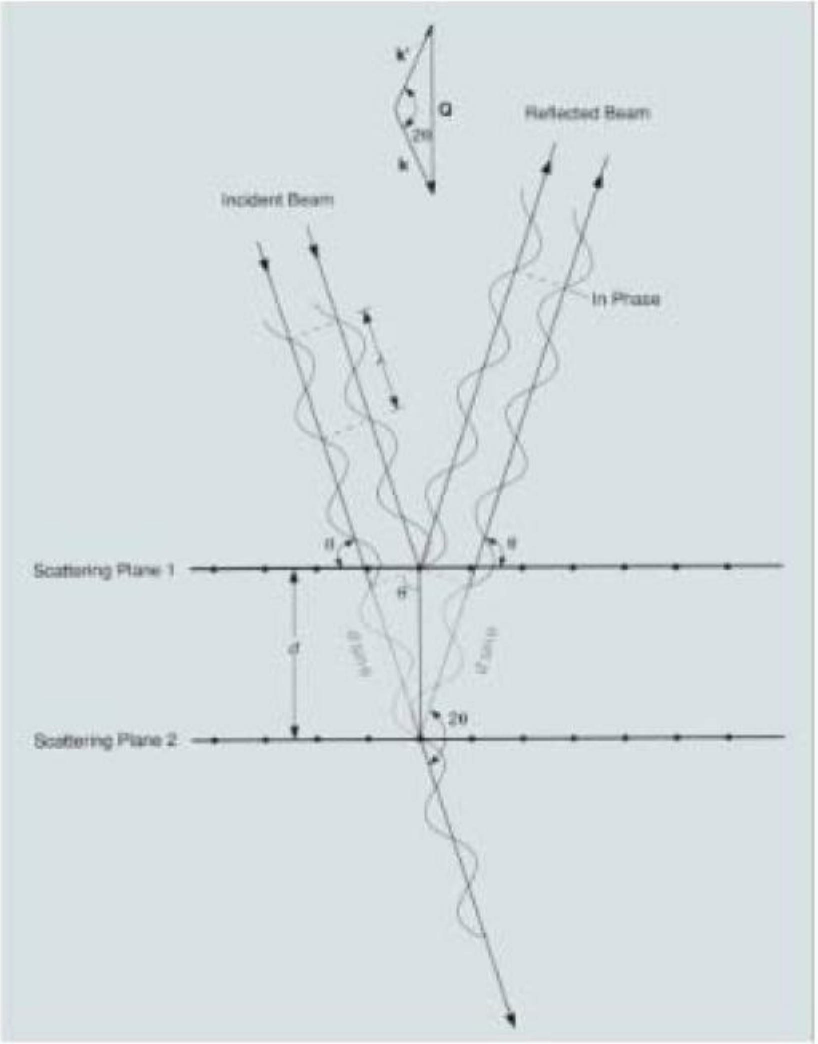
$g(\vec{R})$ and hence $S(q)$ are isotropic.

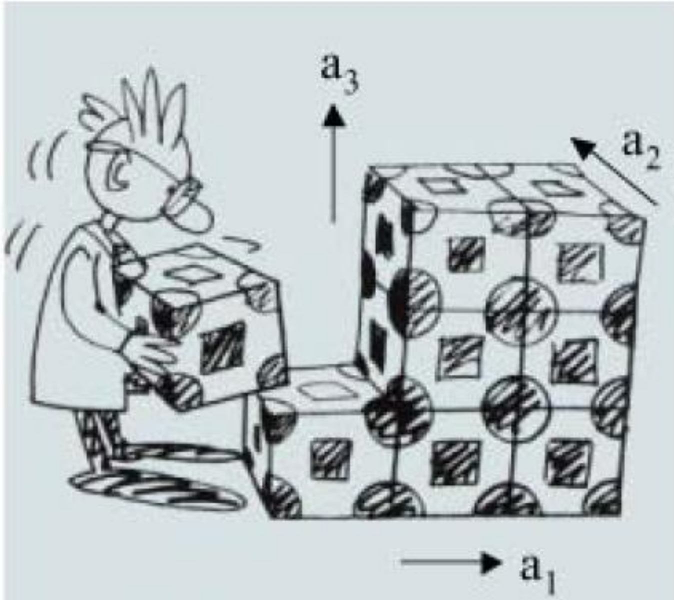
$g_d(R)$ = Reverse F.T. of $[S(q)-1]$

$$=4\pi\int_0^\infty dq\, q^2\,\frac{\mathrm{Sin}(qR)}{(qR)}\left[S(q)-1\right]$$

For Periodic Arrays of Nuclei, Coherent Scattering Is Reinforced Only in Specific Directions Corresponding to the Bragg Condition: $\lambda = 2\, d_{hkl} \sin(\theta)$ or $2\, k \sin(\theta) = G_{hkl}$







unit cell

The repeating unit of a crystal.

Reciprocal Lattice

Lattice Vectors $\quad \bar{R}_\ell = m_1\bar{a}_1 + m_2\bar{a}_2 + m_3\bar{a}_3$

$\bar{a}_1, \bar{a}_2, \bar{a}_3 \rightarrow$ primitive translation vectors of unit cell.

S.K. Sinha

Define 3 other vectors:

$$\boxed{\begin{aligned} \bar{b}_1 &= 2\pi(\bar{a}_2 \times \bar{a}_3)/v_0 \\ \bar{b}_2 &= 2\pi(\bar{a}_3 \times \bar{a}_1)/v_0 \\ \bar{b}_3 &= 2\pi(\bar{a}_1 \times \bar{a}_2)/v_0 \end{aligned}}$$

$$v_0 = \bar{a}_1 \cdot (\bar{a}_2 \times \bar{a}_3)$$
$= $ unit cell vol.

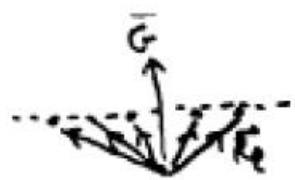
These have the property that $\bar{a}_i \cdot \bar{b}_j = 2\pi\delta_{ij}$

So if we choose any vector $\bar{G}$ on the lattice defined by $\bar{b}_1, \bar{b}_2, \bar{b}_3$:

$$\bar{G} = n_1\bar{b}_1 + m_2\bar{b}_2 + m_3\bar{b}_3$$

then for any $\bar{G}, \bar{R}_\ell$,

$\bar{G} \cdot \bar{R}_\ell = 2\pi \times \text{integer} \rightarrow$ Implies $\bar{G}$ is normal to sets of <u>planes</u> of atoms spaced $2\pi/G$ apart.



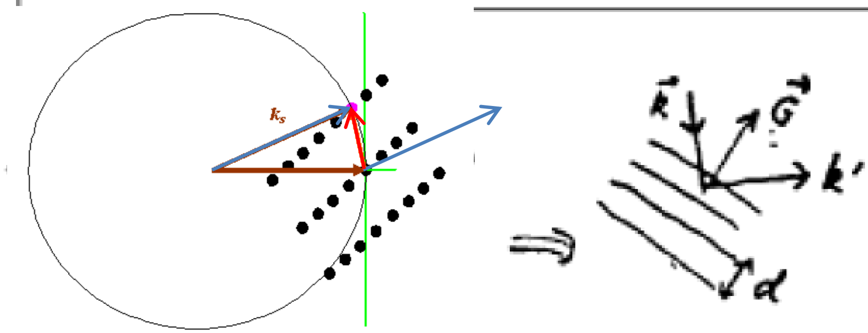
OR

$$\boxed{e^{i\bar{G}\cdot\bar{R}_\ell = 1}}$$

(Introduce e^{-2W} = "Form factor" for thermal smearing of atoms = $e^{-\left\langle (\vec{q}\cdot\vec{u})^2 \right\rangle}$ $\Rightarrow$ Debye-Waller factor)

Similarly,

$$\boxed{\left(\frac{d\sigma}{d\Omega}\right)_{x-rays} = Z^2 r_0^2 \left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right) f^2(\vec{q}) e^{-2W} \; N \cdot \frac{(2\pi)^3}{v_0} \sum_{\vec{G}} \delta(\vec{q}-\vec{G})}$$



Bragg Reflections: $k' - \vec{k} = \vec{G}$

$$2k\,\mathrm{Sin}\,\theta = G = \frac{2\pi}{d}$$

$\rightarrow$ $\boxed{\lambda = 2d\,\mathrm{Sin}\theta}$ Bragg's Law

$$\left(\frac{d\sigma}{d\Omega}\right)_{neutron} = \frac{N\cdot(2\pi)^3}{v_0}\sum_G |F_G|^2 \delta(\vec{q}-\vec{G})$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{x-ray} = \frac{N\cdot(2\pi)^3}{v_0}\sum_G |F_G|^2 \delta(\vec{q}-\vec{G})\left(\frac{1+\mathrm{Cos}^2(2\theta)}{2}\right)$$

where

$$\boxed{F_G = \sum_K Z_K f_K(\vec{G}) r_0\, e^{-2W_K} e^{-i\vec{G}\cdot\vec{R}_K}}$$ – x-ray structure factor

Measurement of Structure Factors → Structure

BUT what is measured is $|F_G|^2$ **NOT** F_G!

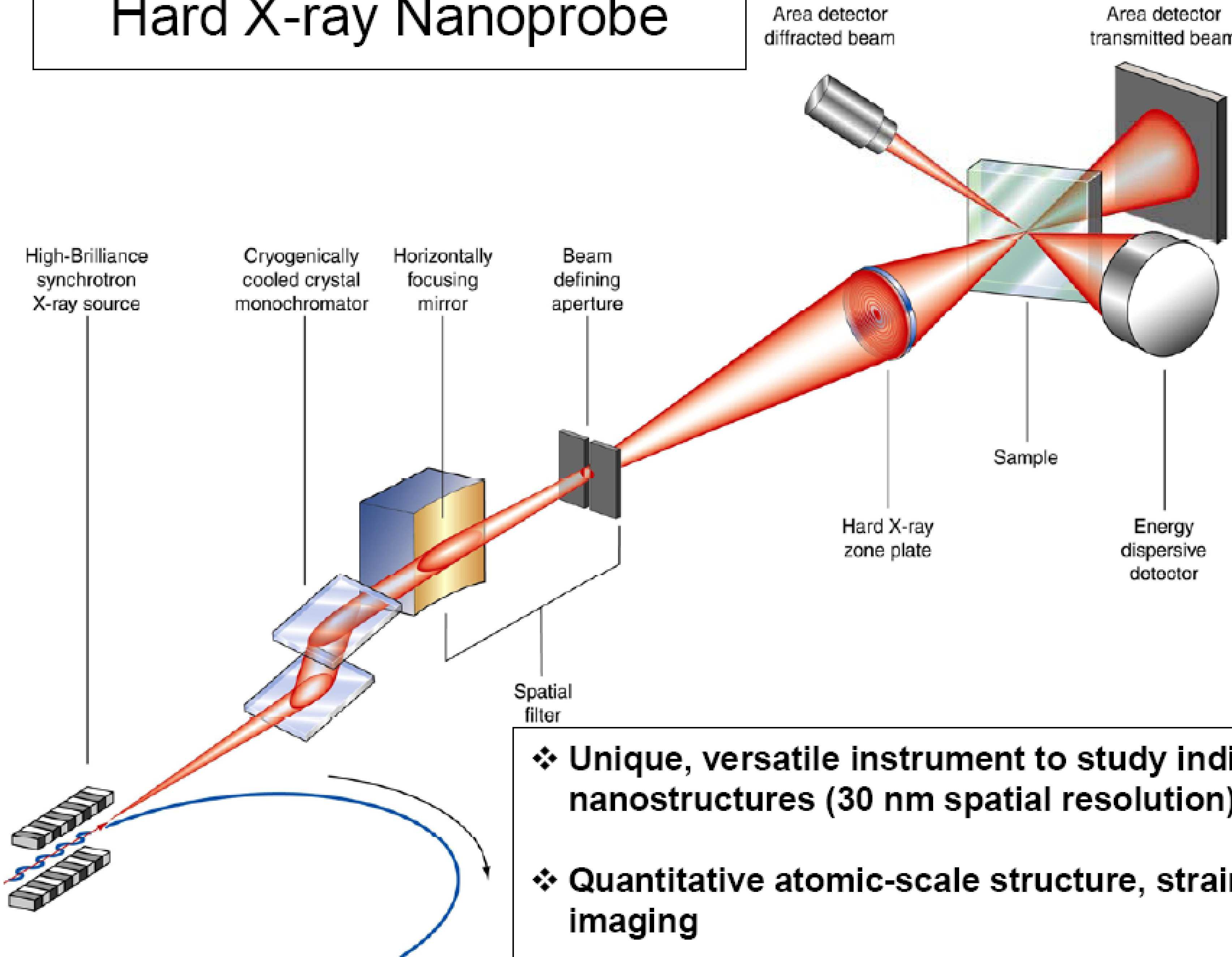
→ "Phase Problem" → Special Methods

Note that $|F_G|^2$ can be written $\sum_{KK'} \mu_K \mu_{K'} e^{-i\vec{G}\cdot(\vec{R}_K-\vec{R}_{K'})}$

so that its F.T. yields information about pairs of atoms

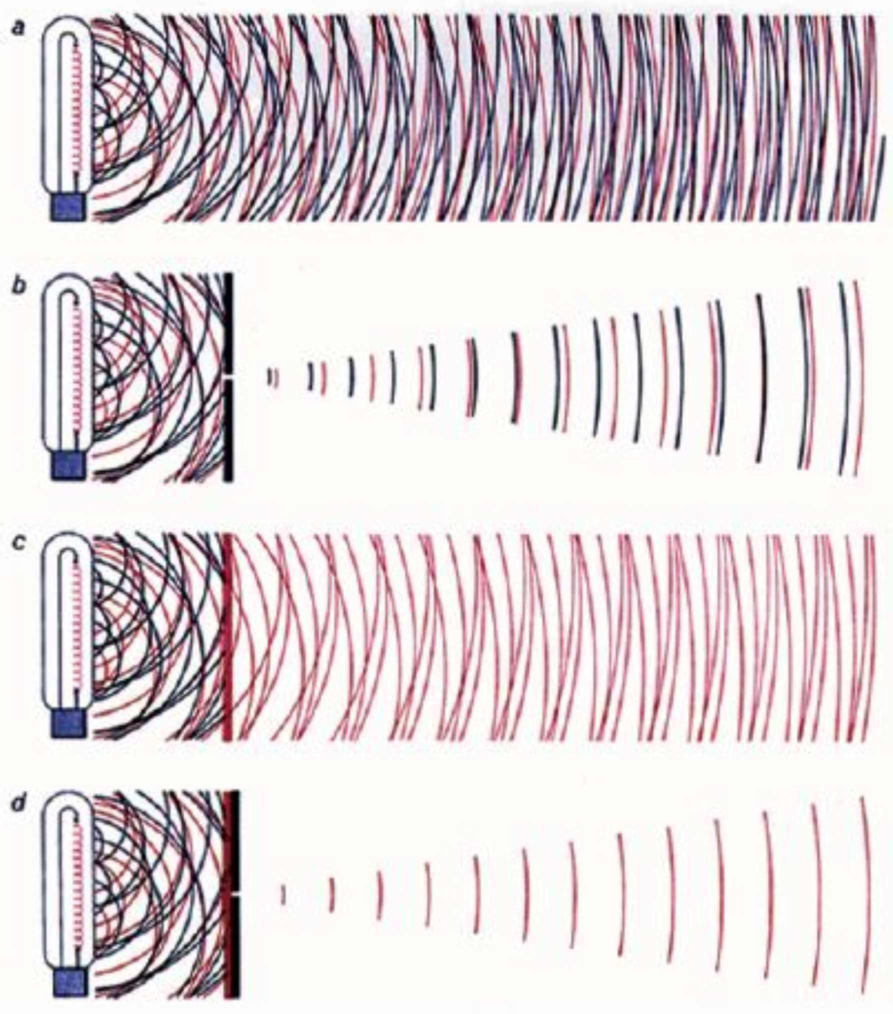
separated by $\vec{R}_K - \vec{R}_{K'} \Rightarrow$ Patterson Function.

Hard X-ray Nanoprobe



- ❖ **Unique, versatile instrument to study individual nanostructures (30 nm spatial resolution)**
- ❖ **Quantitative atomic-scale structure, strain, orienta imaging**

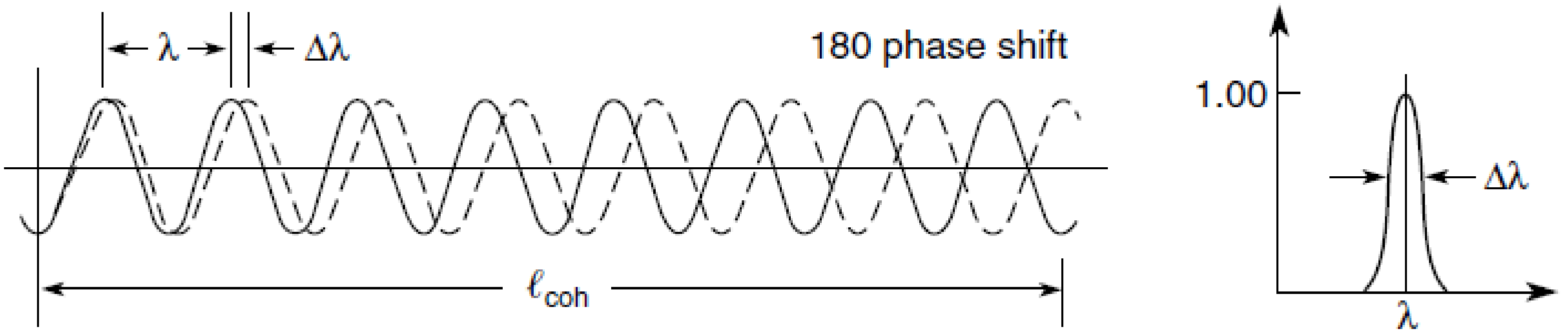
Spatial and Spectral Filtering to Produce Coherent Radiation



Courtesy of A. Schawlow, Stanford.

Spectral Bandwidth and Longitudinal Coherence Length

(Temporal coherence)



Define a coherence length ℓ_{coh} as the distance of propagation over which radiation of spectral width $\Delta\lambda$ becomes 180° out of phase. For a wavelength λ propagating through N cycles

$$\ell_{coh} = N\lambda$$

and for a wavelength $\lambda + \Delta\lambda$, a half cycle less $(N - \frac{1}{2})$

$$\ell_{coh} = (N - \tfrac{1}{2})(\lambda + \Delta\lambda)$$

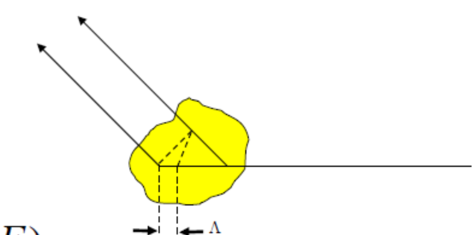
Equating the two

$$N = \lambda/2\Delta\lambda$$

so that

$$\boxed{\ell_{coh} = \frac{\lambda^2}{2\,\Delta\lambda}}$$

$$\Lambda \approx \lambda(E/\Delta E)$$



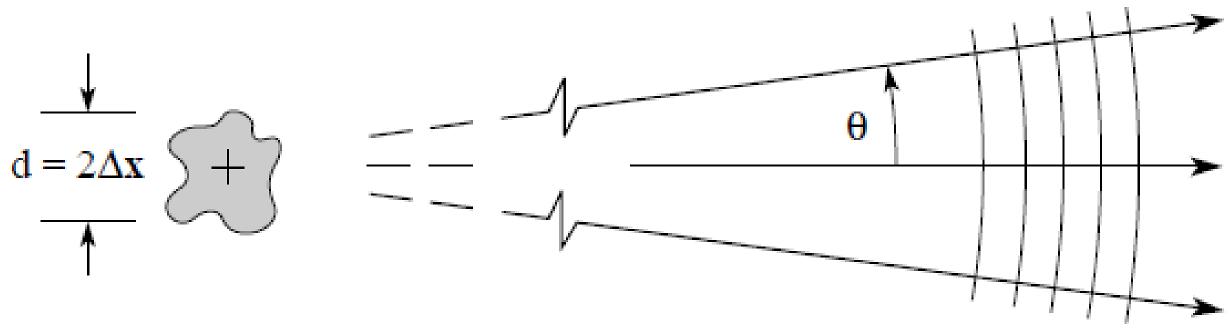
Partially Coherent Radiation Approaches Uncertainty Principle Limits

$\Delta \mathbf{x} \cdot \Delta \mathbf{p} \geq \hbar/2$ (8.4) Standard deviations of Gaussian distributed functions (Tipler, 1978, pp. 174-189)

$\Delta \mathbf{x} \cdot \hbar \Delta \mathbf{k} \geq \hbar/2$

$\Delta \mathbf{x} \cdot \mathbf{k} \Delta\theta \geq 1/2$

$2\Delta \mathbf{x} \cdot \Delta\theta \geq \lambda/2\pi$

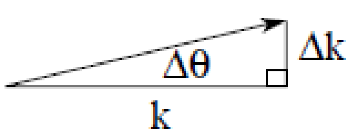


Spherical wavefronts occur in the limiting case

Note:

$\Delta \mathbf{p} = \hbar \Delta k$

$\Delta k = k\Delta\theta$



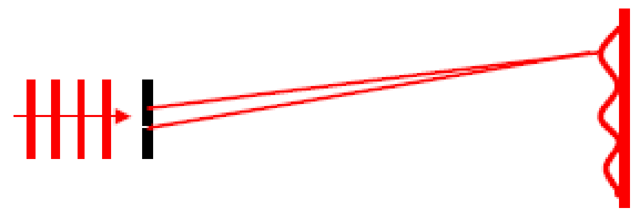
$$\left.\begin{array}{c}\boxed{d \cdot \theta = \lambda/2\pi} \\ \text{(spatially coherent)}\end{array}\right\} \frac{1}{\sqrt{e}} \text{ quantities}$$

or

$$(d \cdot 2\theta)_{FWHM} \simeq \lambda/2 \; \} \text{ FWHM quantities}$$

What is Coherence?

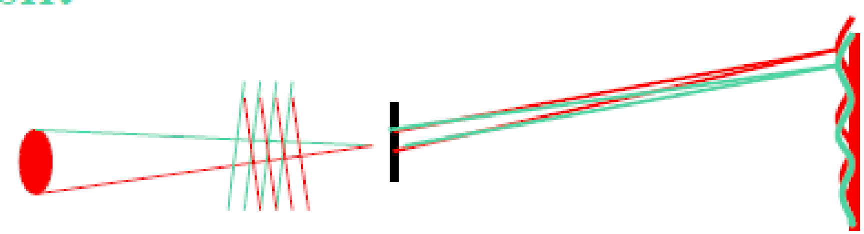
Ideal Young's double slit experiment



Intensity varies as

$$I = 2I_0\left[1 + \cos\left(2\pi d \sin(\theta)/\lambda\right)\right]$$

Real Young's double slit experiment



Intensity varies as

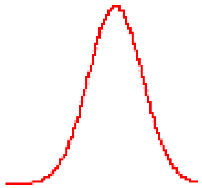
$$I = 2I_0\left[1 + \beta\cos\left(2\pi d \sin(\theta)/\lambda\right)\right]$$

β is the contrast, determined by the angular size of the source

Coherence Length and Contrast

It is generally convenient to assume the source has a Gaussian intensity profile

$$I(x) = \frac{I_0}{\sqrt{2\pi\xi}} \exp\left[-\left(x - x_0\right)^2 / 2\sigma^2 \right]$$



One can then define a coherence length

$$\xi = \frac{\lambda R}{2\sigma\sqrt{\pi}}$$

This characterizes the distance over which two slits would produce an interference pattern, or more generally the length scale over which any sample will produce interference effects.

A more rigorous theory can be found in e.g. Born and Wolf

How Practical is it to Make X-rays Coherent?

Consider a point 65 meters downstream of an APS Undulator A

$$\lambda = 0.2\text{nm}, \quad \Delta\lambda/\lambda = 3\times10^{-4}$$

Ge 111

$$\sigma_{\mathrm{x}} = 254\mu\text{m}, \sigma_{\mathrm{y}} = 12\mu\text{m}$$

$$\xi_x = \frac{\lambda R}{2\sigma_x\sqrt{\pi}} = 14\mu\text{m}$$

$$\xi_y = \frac{\lambda R}{2\sigma y\sqrt{\pi}} = 306\mu\text{m}$$

$$\Lambda = 0.66\mu\text{m}$$

$\sim 3\times10^{10}$ Photons/Coherence Area

Scattering of Coherent X-rays

$$I(Q) \propto \int\int e^{i\vec{Q}\cdot\overrightarrow{r''}} \rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\overrightarrow{r''}\right)d\vec{r}\,d\overrightarrow{r''}$$

For incoherent x-rays the actual scattering represents a statistical average over many incoherent regions within the sample and one obtains:

$$\rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\overrightarrow{r''}\right) \approx \left\langle \rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\overrightarrow{r''}\right)\right\rangle \equiv g\left(\vec{r}\right)$$

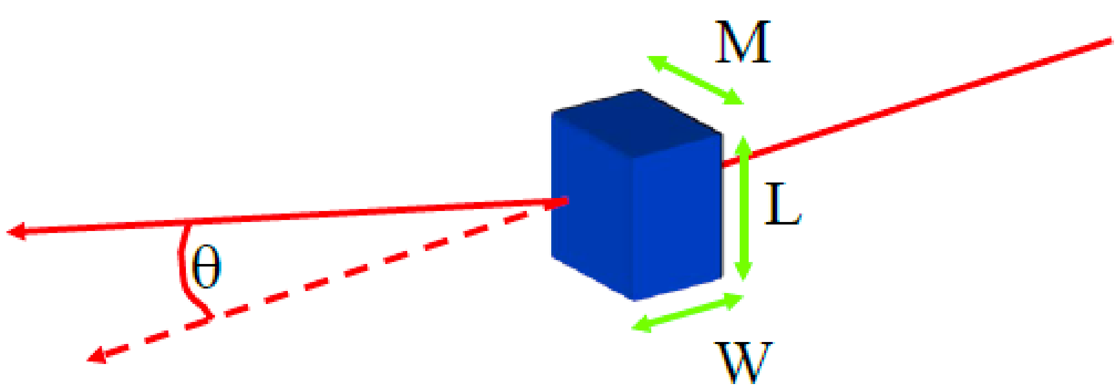
For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.

Speckle Size and Contrast

The speckle widths are approximately the size of the diffraction pattern from a slit the size of the sample:

$$\Delta\theta \sim \lambda / L$$

The contrast is given by the ratio of the scattering volume to the coherence volume, $\Lambda\xi_x\xi_y/MLW\sin(\theta)$

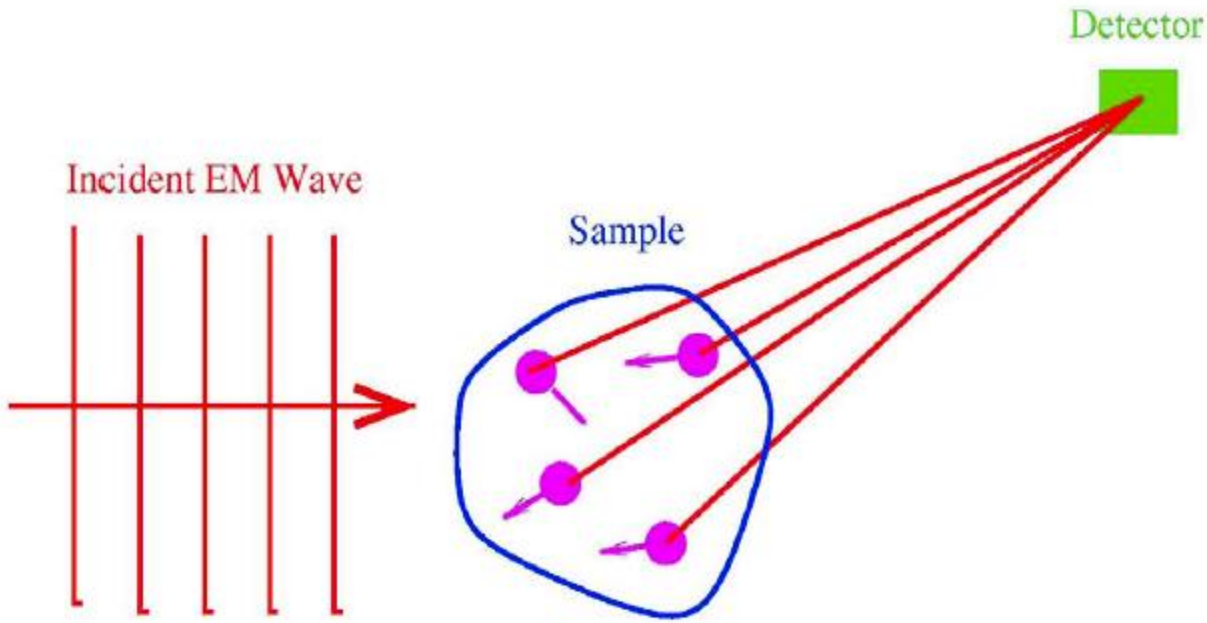


Exact numbers require integrals over the sample volume and electric field spatial correlation function. For small angles, the scattering volume is much smaller than the sample volume.

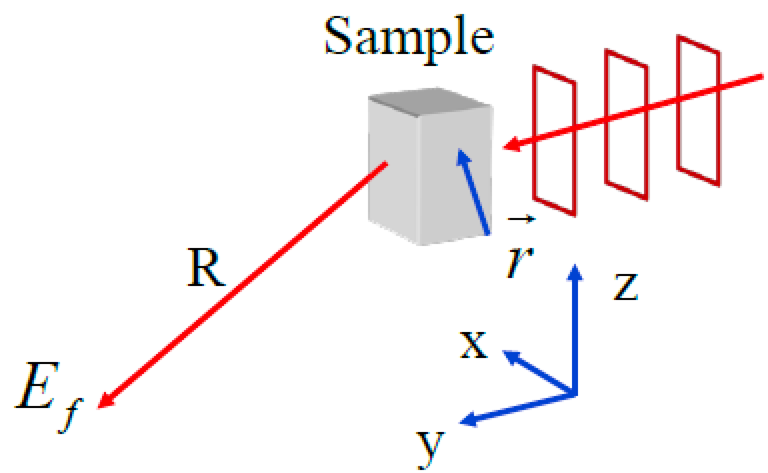
What to do with coherent x-rays?

- Try to invert the speckle to get information about the exact structure factor.
- Ignore the details of the exact structure factor, but use the time fluctuations of the pattern to study dynamics of the material (XPCS)

Measuring Dynamics



The Intensity-Intensity Correlation Function



$$g_2(Q,\tau) \equiv \frac{\langle I(Q,t)\, I(Q,t+\tau)\rangle}{\langle I\rangle^2}$$

How to calculate g_2

- Calculate electric field intensity correlation function at the observation point:

$$G_2(Q,\tau)=\int \exp(iQ\cdot r')\langle E_f^2(r,t)\, E_f^{\,2}(r+r',t+t)\rangle_{r,t}\, dr'$$

- The fourth order correlations in E, can be reduced to pairs of second order correlation functions

- Assume correlation lengths are smaller than sample size, and the scattering can be factored into independent space and time parts.

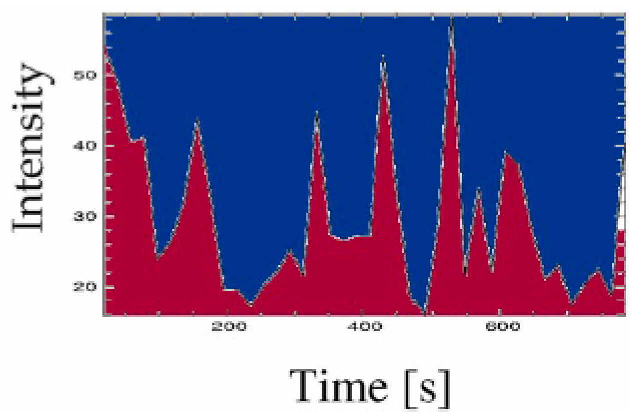
Final Result

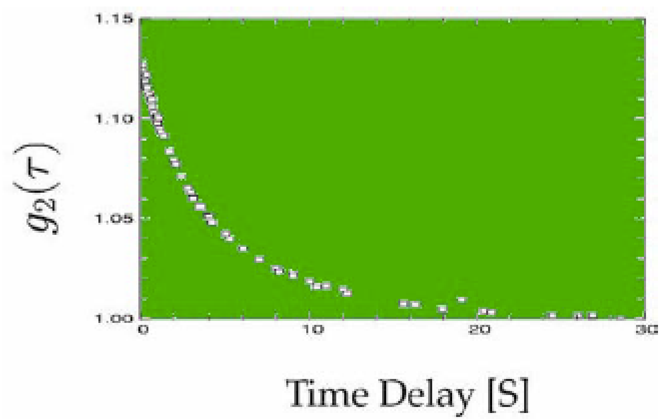
$$G_2(\vec{Q},\tau)=\langle I\rangle^2\left[1+\beta f(Q,\tau)^2\right]$$

The contrast factor, β, is related to the degree of coherence and can be between 0 and 1

$$f(\vec{Q},\tau)=S(\vec{Q},\tau)/S(\vec{Q},0)$$

$$S(\vec{Q},\tau)=\left\langle\int e^{i\vec{Q}\cdot\vec{r}}\rho_e(0,0)\,\rho_e(\vec{r},\tau)\,d\vec{r}\right\rangle$$





For Brownian motion, this can be reduced to an exponential decay proportional to the diffusion coefficient.

$$f(Q,\tau) = e^{-DQ^2\tau}$$

Here, the diffusion coefficient is related to the viscosity, η and the radius a, via the Stoke-Einstein relation:

$$D = k_B T \,/\, 6\pi\eta a$$